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(56) Documents Cited

**None**

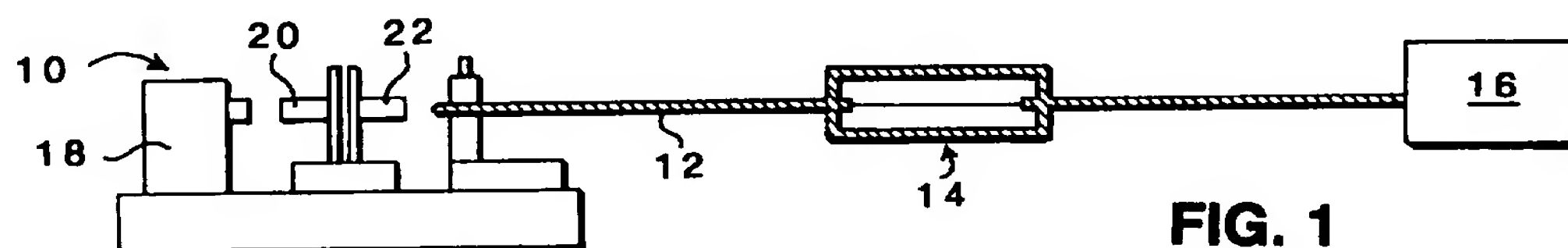
(58) Field of Search

UK CL (Edition N ) **G1A ADEW**

INT CL<sup>6</sup> **G01N 21/78 21/80**

## (54) Waveguide pH sensor

(57) An apparatus for sensing pH comprises a sensor body (14) having a semi-permeable membrane (30) which, in use, contacts a fluid under test. A waveguide, e.g. an optical fibre (12) passes into the interior of the sensor body. The sensor body is filled with a fluid, such as methylene blue dye, in contact with the waveguide whose ionic attraction to the surface of the waveguide varies with pH, thereby varying the evanescent field absorption of radiation passing through the waveguide. Light from a laser light source (10) is transmitted along the waveguide and is detected by a light detector (16). Since the evanescent field absorption varies with pH, the intensity of light detected will also vary with pH.



**FIG. 1**

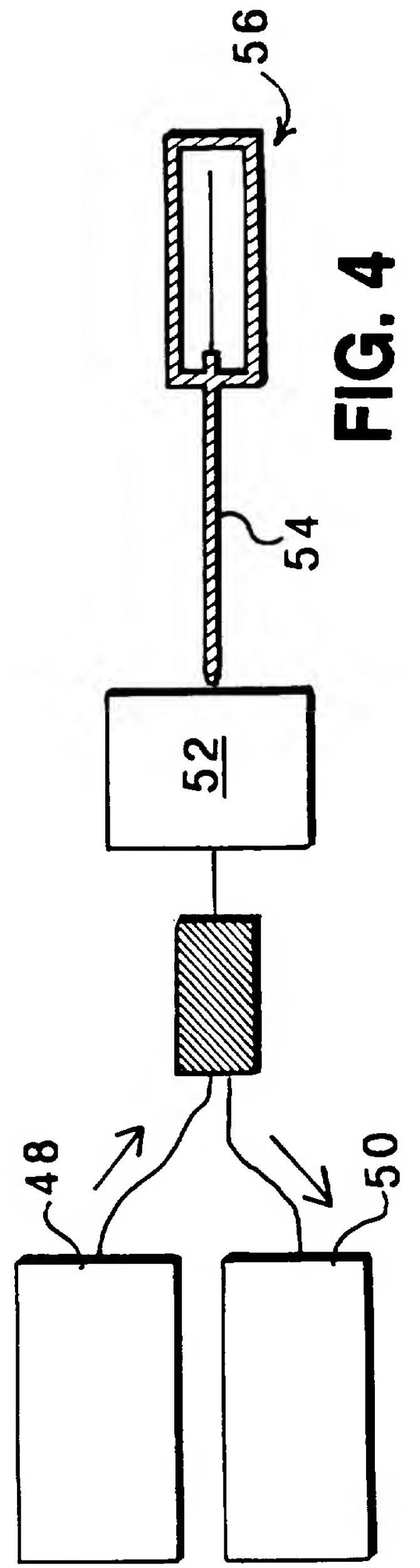
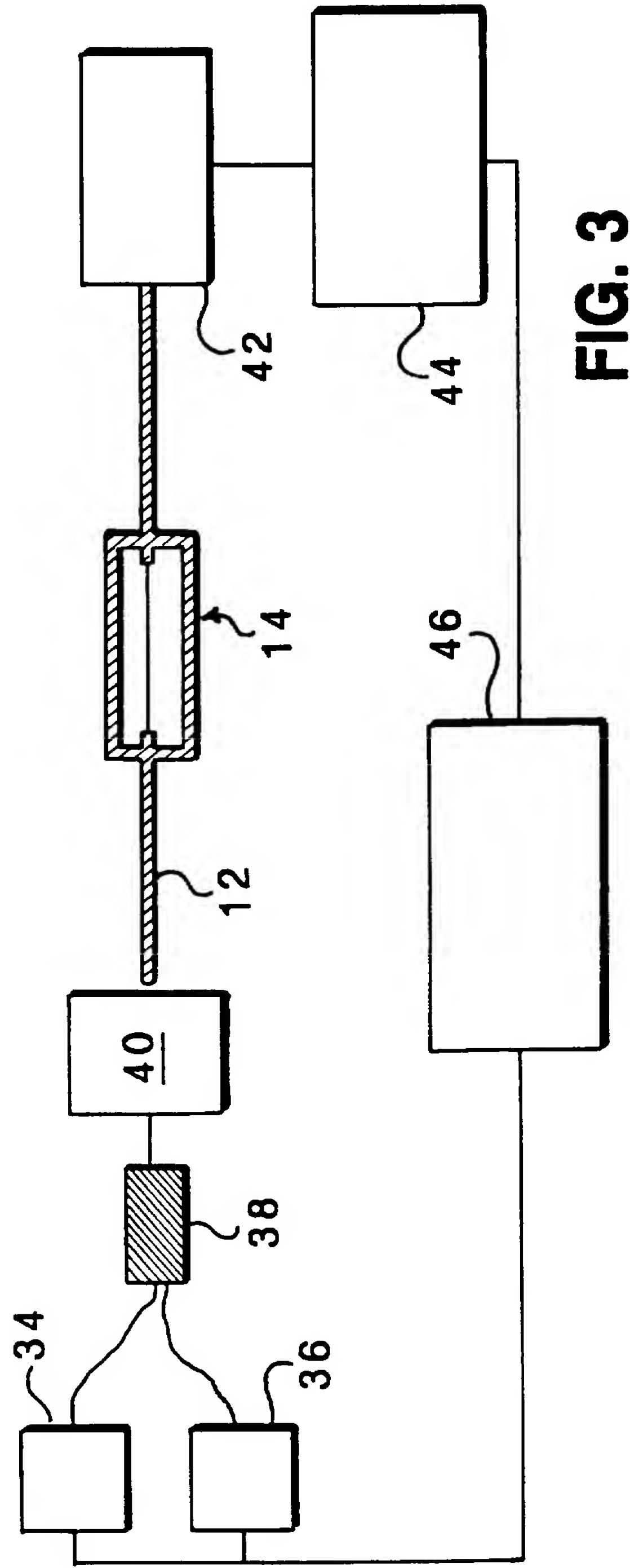
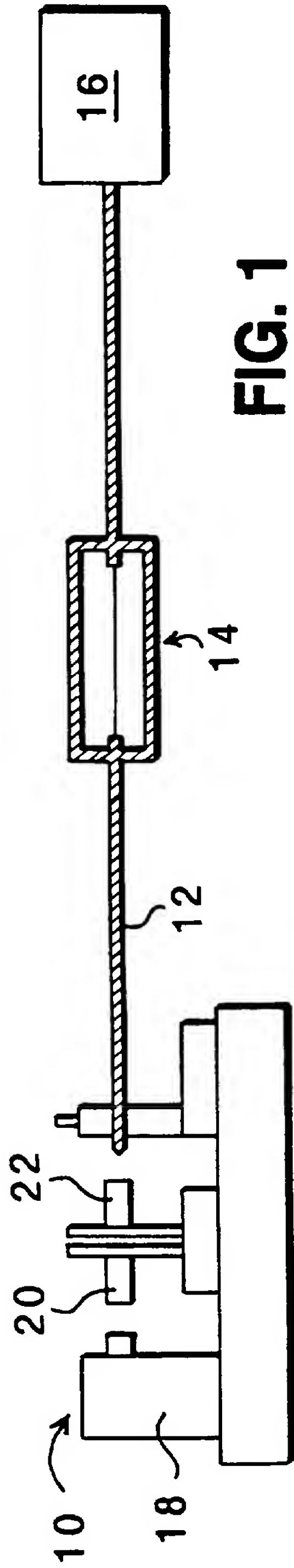


FIG. 2

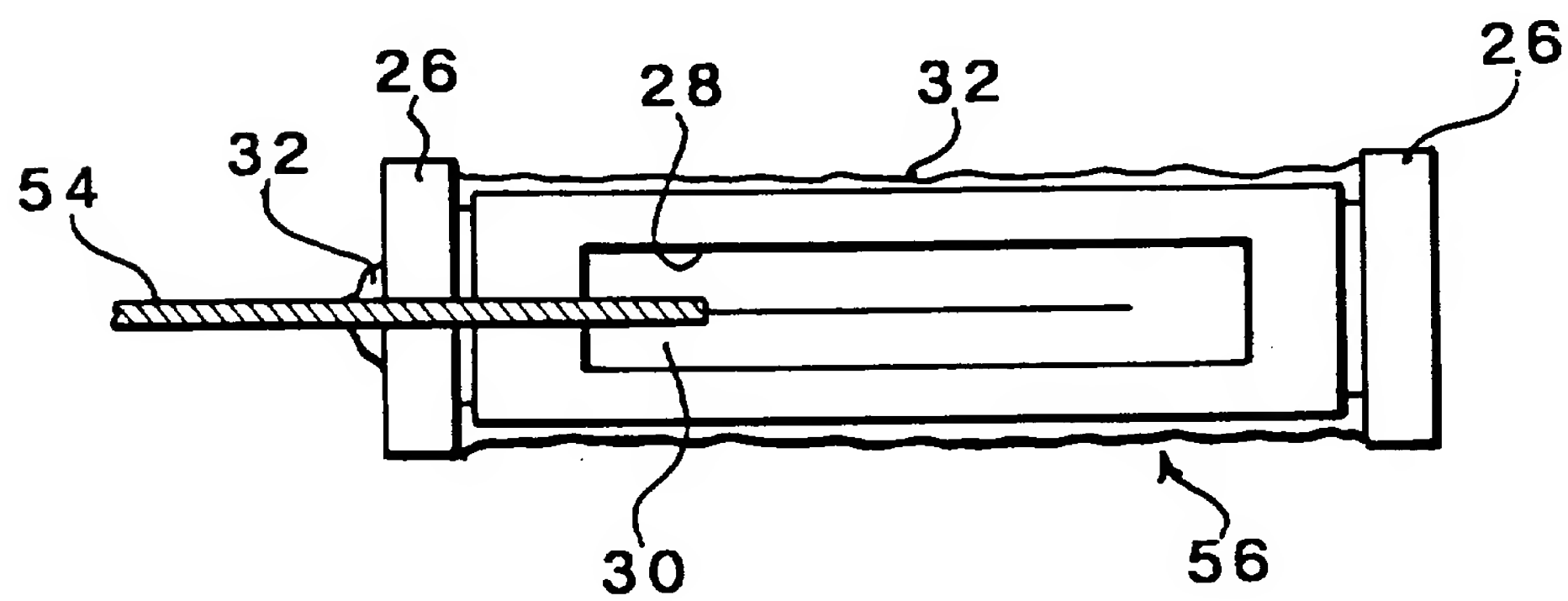
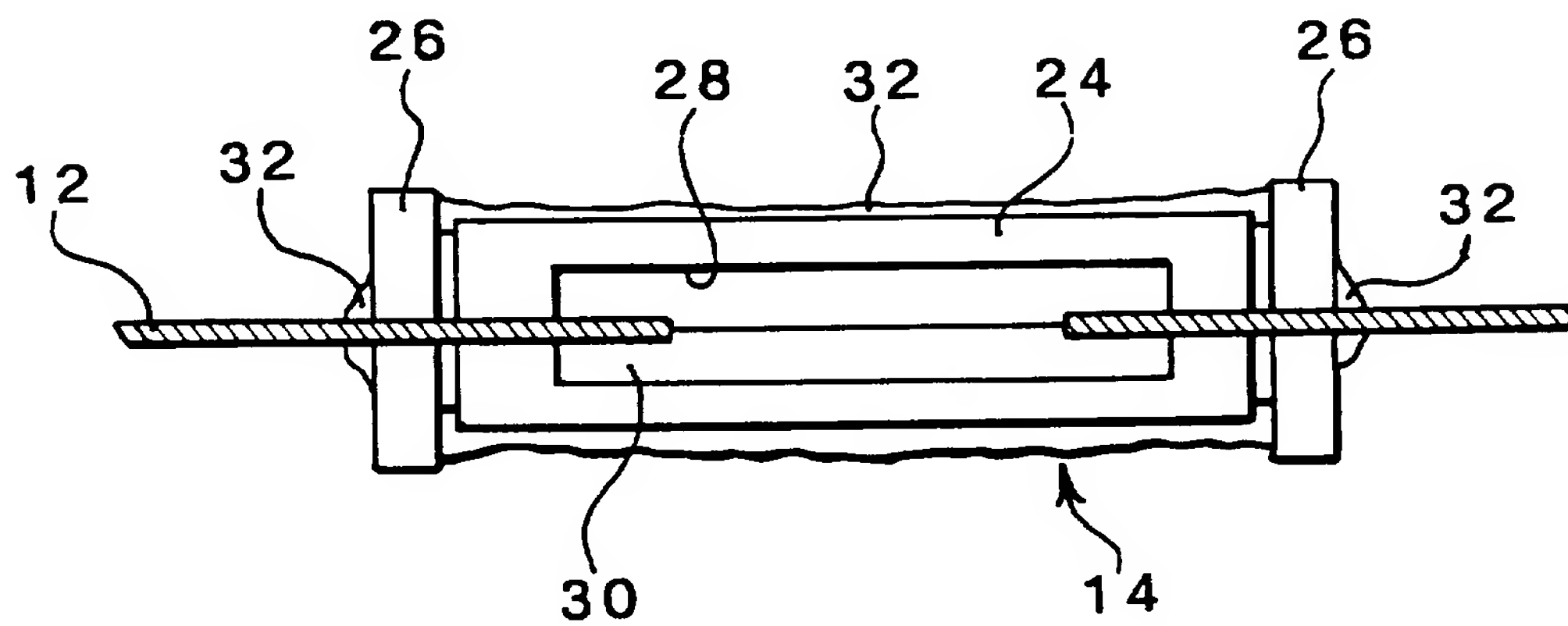


FIG. 5

DESCRIPTIONWAVEGUIDE pH SENSOR

The present invention relates to waveguide pH sensors and in particular, but not exclusively, to optical fibre sensors for measuring pH.

The measurement of pH is of great importance in the case of medical applications (e.g. blood pH) as well as industrial ones (e.g. nuclear reactor monitoring bioreactors and waste water processing). Optical fibre sensors in general offer greater advantage over conventional potentiometric sensors including the possibility of miniaturisation, electrical insulation and immunity to electromagnetic interference. Moreover, they make possible quasi-distributed sensing over large distances (multi-point measurements using only one fibre).

Optical fibre pH sensors designed to date are largely based on monitoring the changes in colour of several immobilised indicators (e.g. bromothymol blue, phenol red, etc) or changes in the fluorescence (e.g. intensity, decay time) of fluorimetric indicators (e.g. acridine, 2-naphtol). Due to their nature, these sensors have a limited range of linear response; typically 2-3pH. This restricts the use of these sensors to highly specialised applications (e.g.

measurement in the physiological range, around pH 7). Also, it is necessary either to take samples from the liquid in question in order for measurement to take place (in which there is a considerable delay before the reading is taken) or for contamination of the liquid undertest by the indicator to be irrelevant.

It is an object of the present invention to provide a waveguide pH sensor which is usable over a wider pH range, and which can give continuous, almost instantaneous measurements of pH without the need to remove samples and without the risk of contamination by indicators.

The present invention makes use of the phenomenon known as evanescent field absorption. At the boundary between two media of different refractive indices forming a waveguide, a portion of the electric field of rays undergoing internal refraction exists beyond the interface. If an absorbing substance is allowed to interact with this field, a subsequent decrease in the power transmitted within the waveguide will occur. The principles of evanescent field absorption are well established. However the present invention relates to the type of interaction between the absorbing medium and the fibre core boundary.

In accordance with a first aspect of the present invention, a pH sensor comprises a sensor body, a

semi-permeable membrane forming part of the sensor body which, in use, contacts a fluid undertest, a waveguide passing into the interior of the sensor body and a fluid within the sensor body in contact with the waveguide whose ionic attraction to the surface of the waveguide varies with pH, thereby varying the evanescent field absorption of radiation passing through the waveguide.

Preferably the waveguide comprises an optical fibre. If an optical fibre is used as the waveguide at least a portion of the cladding layer within the sensing area is removed.

The fluid within the sensor should be of a lower refractive index than that of the waveguide, in order for the evanescent field absorption to occur. One example of fluid which can be used is an aqueous solution of methylene blue dye which can be used with a silica-core optical fibre as a waveguide. As the pH increases the dye is more strongly attracted to the surface of the fibre. Higher pH values lead to an increase in the negative charge on the surface of the fibre due to the  $\text{OH}^-$  ions modifying the silyl groups at the surface, attracting more positively-charged dye molecules. The dye molecules on the surface of the optical fibre core will increase the evanescent field absorption and thus reduce the intensity of radiation

transmitted through the fibre.

Preferably, the sensor body is tubular and the waveguide passes sealingly into the sensor body. In one arrangement the sensor is transmissive in that the waveguide passes through and out of the sensor body and light is transmitted through and detected from the other end of the waveguide. In another arrangement the sensor is a probe-type sensor and relies upon the back reflection of light from a free end of the waveguide within the sensor body.

The wavelength of radiation is preferably chosen to optimise the evanescent field absorption.

In accordance with a second aspect of the present invention an apparatus for measuring pH of a solution comprises a pH sensor in accordance with the present invention, a radiation source for transmitting radiation into the sensor via the waveguide and a detector for detecting the intensity of radiation from the waveguide.

In one embodiment two radiation sources of different wavelength are provided. This is useful if the fluid within the sensor body is a solution, since when solute molecules are attracted to or repelled from the surface of the waveguide, solvent molecules are consequently displaced or attracted as appropriate. By monitoring absorption of radiation

due to the solvent of a different waveguide (which is preferably chosen to maximise evanescent field absorption) and comparing this to the absorption due to the solute it is possible to eliminate common mode noise such as bends in the waveguide and coupling optics drift. For example, for a solution of methylene blue in water two lasers transmitting at 670nm and 1300nm respectively can advantageously be used. If two lasers are used, they are preferably time-multiplexed, the multiplexing signal being used to trigger a signal processing unit.

By way of example only, specific embodiments of the present invention will now be described, with reference to the accompanying drawings, in which:-

Fig. 1 is a side view of a first embodiment of waveguide pH sensor apparatus in accordance with the present invention;

Fig. 2 is a detail side view of the sensor of Fig. 1;

Fig. 3 is a side view of a second embodiment of waveguide pH sensor apparatus in accordance with the present invention;

Fig. 4 is a side view of a third embodiment of waveguide pH sensor apparatus in accordance with the present invention; and

Fig. 5 is a detail side view of the sensor of

Fig. 4.

Referring to Figs. 1 and 2 the sensor apparatus comprises a laser light source 10, an optical fibre 12 leading from the light source 10 through a pH sensor 14 and a light detector 16. The light source comprises a thermally stabilised laser diode 18 which outputs light at constant output power at a wavelength of 670nm (although this wavelength can be selected to be different, as will be explained). The laser light from the laser 18 is collimated by means of a X20 microscope objective 20 and a X40 microscope objective 22 is used to obtain an angular magnification required for beam launching (or, if required, with mode filtering). The optical fibre 12 is a 200 $\mu$ m core polymer-clad silica core (PCS) fibre, but other fibres can be used if desired.

As best seen in Fig. 2, the sensor 14 comprises a stainless steel tube 24 approximately 5cm long sealed at each end with a plastics plug 26. The tube is provided with two rectangular cut-out windows 28 which are sealed by means of an ion-selective semi-porous membrane 30. A suitable membrane 30 is that used in kidney dialysis machines, but different membranes can be selected according to the desired response time. The optical fibre 12 passes into and out of the sensor through the plastics plugs 26 at each end and a layer

of epoxy resin 32 ensures that the sensor is fluid-tight.

As shown schematically in Fig. 2, the cladding of the optical fibre 12 within the sensor 14 is removed to leave a 30nm length of bare silica core within the sensor. The sensor is filled with an aqueous solution of methylene blue dye at a concentration of  $10\mu\text{m}/\text{l}$  to  $190\mu\text{m}/\text{l}$ . The actual concentration can be varied to tailor the sensor to the specific application by selecting the approximate insertion loss (dye absorption sensitivity (dB/pH) ratio). The detector 16 is a conventional silicon detector coupled to an optical power meter.

In use, the sensor 14 is placed in the solution whose pH is to be monitored and the laser 18 and detector 16 are switched on. As the pH of the solution undertest increases the  $\text{OH}^-$  ions pass through the membrane 30. This leads to an increase in the negative charge on the silica core because the  $\text{OH}^-$  ions modify the silyl groups at the surface. The negative charge on the silica core attracts more positively charged methylene blue dye molecules to the surface of the silica core which thus interact with the electric field of the light and alternate the light passing through the fibre optic 12 by evanescent field absorption, thereby reducing the amount of light

sensed by the detector 16. Conversely, as the pH decreases the negative charge on the silica core is also decreased, thus resulting in less dye being attracted to the surface of the core and reducing the loss of light out of the core.

In the specific example given the apparatus is effective in measuring pH values from 3 to 10. At pH values outside this range the silica is said to be saturated and no longer interacts with the hydroxide ions.

The relationship between pH and absorption of light by the methylene blue dye is approximately linear over the working range of the sensor. Thus, by appropriate calibration of the detector a value of the pH can quickly and easily be made.

A second embodiment of the present invention is illustrated in Fig. 3. The apparatus comprises a first laser diode 34, identical to that of the first embodiment, which generates light at a wavelength of 670nm and a second laser diode 36 which generates light at a wavelength of 1300nm. The two lasers 34,36 have their outputs coupled together using an optical fibre coupler 38 and the light output of the coupler 38 is collimated and undergoes angular magnification by passing through the same microscope objectives 20,22 (illustrated schematically as 40) in Fig. 3 as

for the first embodiment. The apparatus is also provided with a detector 42, and a signal processor 44 and a multiplexer 46 connected to the detector 42 and the lasers 34,36 respectively and to each other.

Two sources of light at different wavelength are used because when dye molecules are attracted to the surface of the silica core they replace water molecules. By monitoring the absorption due to water at around 1300nm and correlating this absorption due to the methylene blue at 670nm it is possible to eliminate any common mode noise (resulting from, for example, bends in the fibre or coupling optics drift) and to compensate by on-line calibration for aging and surface contamination of the sensor.

To provide measurements at both wavelengths the laser diodes are time-multiplexed, the multiplexing signal being used to trigger the signal processing unit.

A third embodiment of the invention is shown in Fig. 4. This apparatus comprises a laser 48 (identical to the laser 10 of the first embodiment) whose output is linked to the input of a detector 50 (identical to the detector 16 of the first embodiment) by means of an optical fibre coupler. The output from the optical fibre coupler is collimated and undergoes angular magnification by passing through the same

microscope objectives 20,22 (shown schematically as 52 in Fig. 4) as for the first embodiment. The light from the launch optics 52 is transmitted along an optical fibre 54 which is identical to that of the first embodiment except that it only passes through one plastic plug of a sensor 56 and terminates inside the sensor 56.

As best seen in Fig. 5, the sensor 56 is virtually identical to that shown in Fig. 2 and the same reference numerals have been used where appropriate. The only difference is that the optical fibre terminates within the sensor body and does not pass completely through the sensor. The light transmitted along the fibre is back scattered at the free end by means of Fresnel reflection. Absorption due to the methylene blue (which, as described previously, is pH-dependent) affects both the forward and backward propagating evanescent field. The light reflected from the end of the fibre is transmitted back along the fibre and its intensity is measured by the detector 50.

This embodiment is particularly suitable where a transmissive system (i.e. access to both ends of the optical fibre) is impractical, such as in vivo blood measurements where the probe configuration of Fig. 5 is more appropriate.

It would also be possible to improve the performance of the third embodiment by depositing a mirrored surface at the sensing end of the fibre, thus increasing the back scattered light signal. It would also be possible to modify the third embodiment by having two lasers producing light at different wavelengths, as in the second embodiment.

The invention is not restricted to the details of the foregoing embodiments.

For example, different types of optical fibre may be used. The fluid within the sensor may also be different, as long as its ionic attraction to the waveguide varies with pH and as long as its refractive index is less than that of the waveguide, in order to produce the evanescent field absorption. The wavelength of radiation used, however, should be selected to optimise the absorption of radiation by the fluid.

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CLAIMS

1. A pH sensor comprising a sensor body, a semi-permeable membrane forming part of the sensor body which, in use, contacts a fluid under test, a waveguide passing into the interior of the sensor body and fluid within the sensor body in contact with the waveguide whose ionic attraction to the surface of the waveguide varies with pH, thereby varying the evanescent field absorption of radiation passing through the waveguide.

2. A pH sensor as claimed in claim 1, wherein the waveguide comprises an optical fibre.

3. A pH sensor as claimed in claim 2, wherein at least a portion of the cladding layer within the sensing area is removed.

4. A pH sensor as claimed in any of the preceding claims, wherein the ends of the waveguide are located outside the sensor body such that the waveguide passes through the sensor body.

5. A pH sensor as claimed in any of claims 1 to 4, wherein the waveguide terminates inside the sensor body.

6. A pH sensor as claimed in any of the preceding claims, wherein the fluid within the sensor body is of a lower refractive index than that of the waveguide.

7. A pH sensor as claimed in claim 6, wherein the fluid comprises methylene blue dye.

8. A pH sensor as claimed in any of the preceding claims, wherein the sensor body is tubular and the waveguide passes sealingly into the sensor body.

9. A pH sensor as claimed in any of the preceding claims, wherein the semi-permeable membrane forms part of the wall of the sensor body.

10. An apparatus for measuring pH of a solution comprising a pH sensor as claimed in any of the preceding claims, a radiation source for transmitting radiation into the sensor via the waveguide and a detector for detecting the intensity of radiation from the waveguide.

11. An apparatus as claimed in claim 10, wherein the radiation source comprises a laser LED or laser diode.

12. An apparatus as claimed in claim 10 or claim 11, comprising two radiation sources of different wavelengths.

13. An apparatus as claimed in claim 12, comprising a multiplexer and a signal processing unit, the two sources of radiation being time-multiplexed and the multiplexing signal being used to trigger the signal processing unit.

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Application No: GB 9420534.1  
Claims searched: all

Examiner: Gareth Griffiths  
Date of search: 6 December 1995

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.N): G1A (ADEW)

Int CI (Ed.6): G01N 21/78, 21/80

Other: Online Database: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
	NONE	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.